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MASS TRANSFER NEAR A
PYROLYTIC GRAPHITE-GASEOUS INTERFACE

PAUL D. LINDQUIST

TECHNICAL REPORT AFAPL-TR-65-58

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AUGUST 1965

AIR FORCE AERO PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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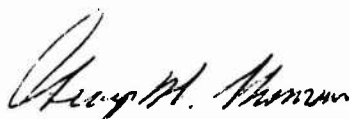
PAUL D. LINDQUIST

FOREWORD

This report was prepared by the AF Aero Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, with Paul D. Lindquist acting as project scientist. The work reported herein was done under Project 3141, Task 314101, "Electrothermal Propulsion."

This work was originally presented in partial fulfillment of the requirements for the degree of Master of Science at The Ohio State University. The author wishes to thank and acknowledge Professor Jones of The Ohio State University for advice given. The assistance of P. Schliesser, U. Martin, and R. Miller of AFAPL is gratefully acknowledged.

This report covers research accomplished from January through May 1965. This report was submitted by the author June 1965.

This technical report has been reviewed and is approved.

GEORGE W. SHERMAN
Chief, Aerospace Power Division
Air Force Aero Propulsion Laboratory

ABSTRACT

This report presents the results of an investigation into the mass loss rate from a pyrolytic graphite foil at various temperatures and pressures. The mass loss in a hydrogen atmosphere is presented at temperatures from 3000 to 4100°R and pressures from 830 to 1550 Torr. The mass loss rate in an inert helium atmosphere at the same temperatures and at pressures from 10^{-3} to 1550 Torr is presented. The experimental data is compared to the theoretical rate and, when applicable, to the work of previous experimenters.

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

NOMENCLATURE

m	mass	lbs
r	mass loss rate	gms/cm^2-sec
r_A	mass diffusion rate of species A	gms/cm^2-sec
r_{A1}	mass loss rate obtained by author	gms/cm^2-sec
r_{A2}	mass loss rate from literature	gms/cm^2-sec
r_B	mass diffusion rate of species B	gms/cm^2-sec
y_2-y_1	boundary layer thickness	ft
A	area	ft^2
C_A	concentration of species A	lb-mole/ft^3
C_B	concentration of species B	lb-mole/ft^3
D_o	diffusivity at standard conditions	ft^2/sec
D_v	mass diffusivity	ft^2/sec
K	thermal conductivity	BTU-ft/hr-ft^2-°F
L	length	ft
M	molecular weight	
P	total pressure	lbs/ft^2
P_A	partial pressure of species A	lbs/ft^2
P_{A2}	partial pressure of A outside boundary layer	lbs/ft^2
P_{A1}	partial pressure of A at graphite surface	lbs/ft^2
P_B	partial pressure of species B	lbs/ft^2
P_v	vapor pressure	Torr
R	gas constant	ft^3-Torr/mole-°R
R'	resistance	ohms
T	temperature	°R
r_{At}	total diffusion of species A	gms/cm^2-sec
α	evaporation coefficient	dimensionless

ρ	mass density	lbs/ft^3
θ	time	secs
σ	electrical resistivity	ohm-ft

Subscripts

| a | | "a" direction in graphite |
| c | | "c" direction in graphite |

SECTION I

INTRODUCTION

The interest in high-temperature materials has increased in recent years because of reentry problems, reactors, space propulsion, heat shielding, and various other applications. One material which has recently come under increased investigation is pyrolytic graphite, a highly oriented crystalline form of carbon. If this material is to be used over an extended period of time, it is necessary that we know the mass transfer rate from the surface of the graphite in the presence of various ambient gases as well as in a vacuum. The effect of mass loss can be deleterious to any system: some typical effects are erosion of heat shielding, changes in properties of critical resistance elements, changes in sizing, or redeposition of carbon at undesired locations. The rate of mass loss is primarily a function of the gas species, temperature, pressure, and flow conditions.

Pyrolytic graphite is not a new material; an early patent was granted to its manufacturer in 1880 (1)*. In the form of filaments it has been known since the turn of the century, when it was used in some very early manufacturing of light bulbs. The innovation of the tungsten filament discouraged its further development. Thereafter, until recently, its properties have been studied merely out of scientific curiosity on a very limited basis.

Pyrolytic graphite is a polycrystalline form of carbon with a well-oriented structure. It is formed when carbon is deposited on a surface by decomposition of a carbonaceous gas at very high temperatures. The resulting material contains no binder, has a high purity, and has a density that normally exceeds 99.5% of the theoretical density of graphite.

The following properties make it a material of interest:

a. Highly anisotropic thermal properties with low thermal conductivity normal to the deposition plane. The conductivity parallel to the deposition surface is approximately 200 times greater than in the normal direction. Room temperature values are typically 1.2 BTU-ft/ft^2/hr/$^\circ$F in the "c" (normal) direction and 290 BTU-ft/ft^2/hr/$^\circ$F in the "a-b" (parallel) direction (see Figure 1).

b. Electrical properties such that it acts as an insulator in the "c" direction and a very good conductor in the "a-b" direction.

c. The best high-temperature strength of any known material.

d. A high strength-to-weight ratio.

The effective utilization of any material requires a knowledge of its properties under various ambient and elevated temperature conditions and an understanding of its limitations, together with a fundamental knowledge of the process variables which produce desired properties. There is in the literature significant amounts of data concerning the reaction of carbon with oxygen, carbon dioxide, and water vapor. The reaction of hydrogen with pure graphitic carbon has not been investigated as thoroughly. This is a potentially important area, however, because hydrogen is often used as a working fluid. A typical example of this would be electrothermal space propulsion devices for which hydrogen, because of its low molecular weight, is a natural propellant. These engines are typically designed for long duration use at high temperatures; therefore, any erosion or ablation of engine materials is of critical importance.

Remarkably few studies have been reported on the direct action of hydrogen on carbons or graphites. In late 1961 Kurt Hedden in a paper presented at the Fifth Conference on Carbon (2) writes "In my opinion no study on the reaction of hydrogen with pure graphitic carbon has been published."

*Numbers in parentheses designate References.

The experiment on which he then reported was concerned with the formation of a specific product, methane, in the temperature range from 2300-2750°R and at very high pressures, 10-100 Atmospheres.

The study herein reported was therefore undertaken to determine the reaction rate of hydrogen with pyrolytic graphite as well as only the sublimation rate of the pyrolytic graphite in an inert helium atmosphere. Since our primary concern is with the mass loss from the graphite, the products of re-action in their various hydrocarbon forms are not differentiated. The temperatures investigated were 3000, 3600 and 4100°R at pressures of 10^{-3}, 30, 830, 1150 and 1550 Torr (mm of Hg). The temperature and pressure variables are considered separately and their influences are determined independently. The flow rates maintained were very low, consequently essentially static conditions existed. The test gas was analysed for impurity content, and the influence of impurities on the test results was also studied.

SECTION II

DISCUSSION OF PYROLYTIC GRAPHITE MATERIAL

It is necessary to examine the method of production of pyrolytic graphite and its general makeup in order to better understand the results and their application.

Pyrolytic graphite, as has been previously indicated, is highly anisotropic due to its formation. It is deposited in layers of crystallites on a heated mandrel in a hydrocarbon atmosphere. The carbon atoms are held together by strong chemical bonds within each plane, and the planes are held together by relatively weak bonding forces. This is depicted schematically in Figure 1. Depending on the temperature of deposition, usually above 4500°R, individual crystallites are deposited in well oriented layers in the "a" direction. There appears to be some rotation about the "c" axis and random translation along the "a-b" plane (3).
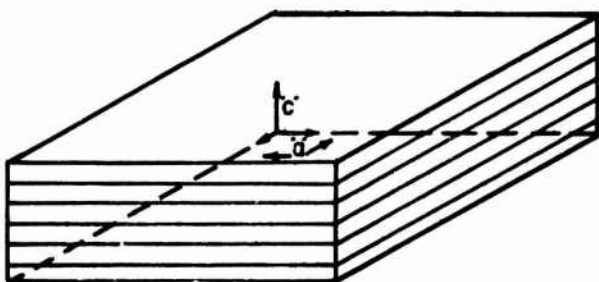

Figure 1. Orientation Directions Of Pyrolytic Graphite

Physical and mechanical properties in pyrolytic graphite vary greatly with respect to orientation. Thermal conductivity in the "a" direction is approximately 200 times that in the "c" direction. At room temperature, pyrolytic graphite has a higher heat conductivity in the "a" direction than does copper, and in the "c" direction it is a better insulator than phenolic plastic. The variations in properties with temperature are shown in Figure 2. Both K_a and K_c decrease with temperature and at approximately equal rates.

All the mechanical properties of pyrolitic graphite vary with direction. Some of these values are presented in Table 1. It should be noted that the sublimation temperature, vapor pressure equals one atmosphere, occurs at 7060°R, which makes this material very appealing for high-temperature applications. Many of the properties are listed only for reference, however, and will only be discussed insofar as they pertain to, or have an effect on, the experiment at hand.

The density of the material can be varied over a wide range by altering the deposition temperature; since the anisotropy tends to lessen with decreasing density, this characteristic is quite significant. The theoretical density of perfect graphite is 2.25 gm/cc. Ordinary commercial graphites will vary from 1.5 to 1.8, however, and densified graphites will vary from 1.7 to 2.0. Pyrolytic graphites have been prepared with measured densities as high as 2.22 (4). The increase in density with increase in temperature of preparation is due to a higher degree of crystallite orientation at higher temperatures. Densities as low as 1.35 gm/cc have been obtained at lower deposition temperatures.

The particular hydrocarbon used to form the pyrolytic graphite also has an effect on the final product. This factor, however, is not nearly as important an effect as deposition temperature and can be neglected(5).

The deposition temperature of a particular graphite material should always be known before the material is used in a given application. The variation of several properties with deposition temperature is shown in Table 2. National Carbon Corp. demonstrated with their Parma arc-torch facility that the ablation resistance of a coating of pyrolytic graphite doubles when the deposition temperature is increased from 3732 to 4100°R (6). This effect is related primarily to the anisotropy of thermal conductivity. The rate of ablation of pyrolytic graphite from a stagnation point is influenced by the thickness

of the coating as well as the thermal con-
ductivity. The thicker coatings because
of their greater heat conductance further
reduce the ablation losses.

The smooth surfaces and anisotropy of
pyrolytic graphite would lead one to suspect
it to have a reaction rate different from
ordinary commercial graphite. This is
indeed the case in the oxidation of graphite
(7), as shown in the plot of oxidation erosion
for the two types of graphite in Figure 3.
In commercial graphites, surface roughness
and microscopic imperfections tend to in-
crease the effective surface area available
for reaction with the ambient gas. In
addition isotropy as well as solid impurities
tend to increase the oxidation rate of ordinary
graphite. It is therefore postulated that the
reaction rate of ordinary graphite with hy-
drogen will show a similar trend.

Tests indicate that the sublimation rate
of pyrolytic graphite is greater from the
"c" surface than from the "a" surface.
Folweiler and Diefendorf investigated the
evaporation rate from both edge and face
surfaces of pyrolytic graphite samples as a
function of temperature only, at 10 atm.
nitrogen pressure. Their findings indicated
a significant difference between sublimation
in one plane as compared to the other (8).

The test material used in the experiment
reported herein was foil 0.010 inch thick.
The test strips were 1/4 x 4 inches, so
the "a" surface area exposed is much
greater than the "c" surface. The results
reported herein are therefore essentially
based on the "a" surface. This gives
more accuracy to the experiment and, since
it is probable that this would be the surface
exposed in most applications, it gives the
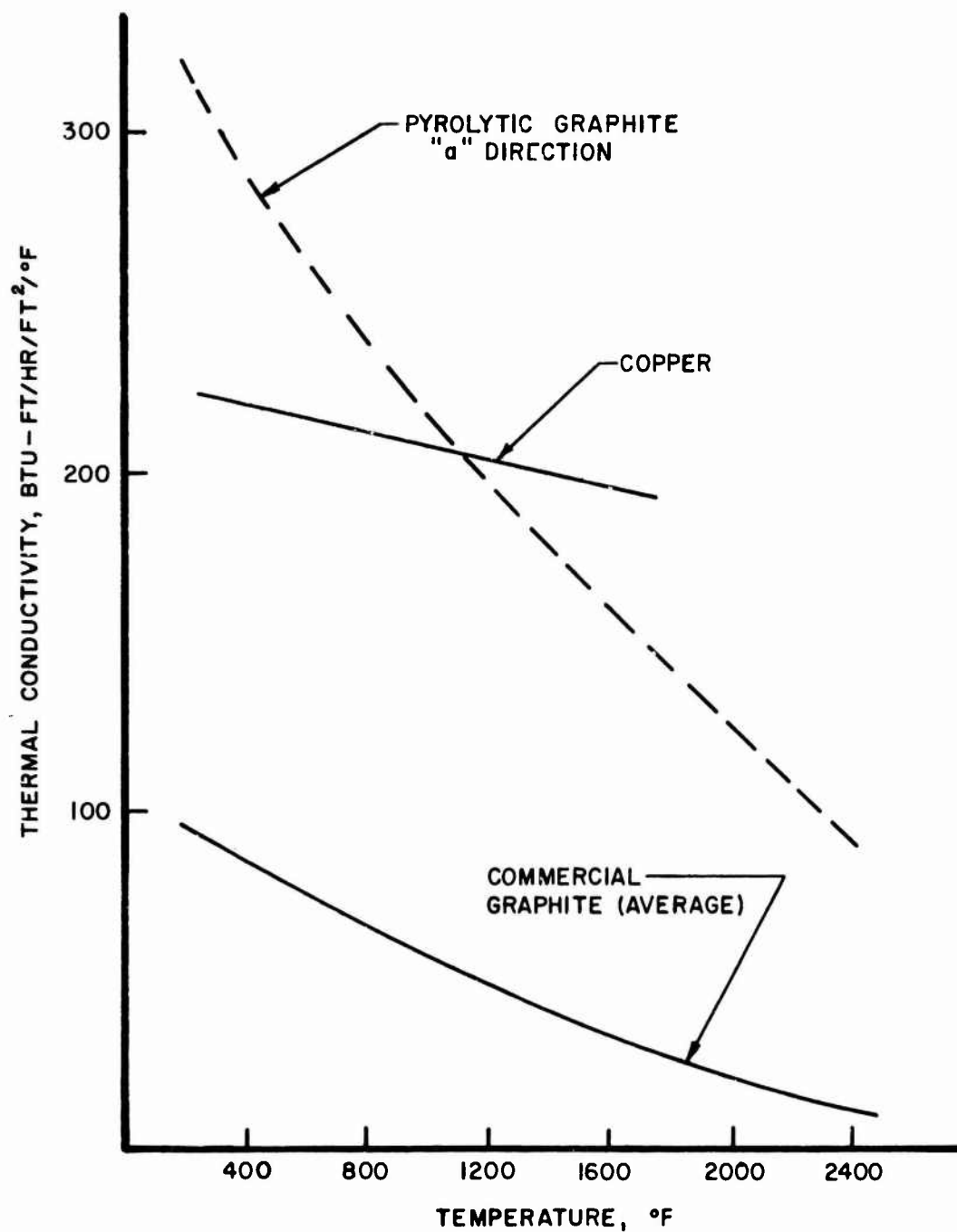most meaningful and useful results.

Figure 2. The Influence of Temperature on the Thermal Conductivity of Graphite

TABLE 1

PROPERTIES OF PYROLYTIC GRAPHITE*

PROPERTY	TEMPERATURE	DIRECTION	
		"a-b"	"c"
Tensile Strength PSI	Room Temp.	15,000	1,500
	5,000° F	60,000	500
Compressive Str. PSI	Room Temp.	15,000	60,000
Youngs Modulus PSI	Room Temp.	5×10^6	1.5×10^6
	4,000° F	2×10^6	0.5×10^6
Poisson's Ratio	Room Temp.	0.2	1.00
Elongation	5,000° F	70-100%	----
Thermal Expansion IN/IN-° F	Room Temp.	0.1×10^{-6}	13×10^{-6}
	5,000° F	3.0×10^{-6}	13×10^{-6}
Thermal Conductivity BTU/ft-Hr. -° F	Room Temp.	280-300	1.2
	2,000° F	80-120	0.6
Emissivity (Integrated)	1,500° F	0.6	0.5
	4,000° F	0.9	----
Electrical Resis. OHM-CM	Room Temp.	5×10^{-4}	0.5
	2,000° F	4×10^{-4}	0.2
Sublimation Point	6,600° F	----	----
Heat of Vaporization	25,700BTU/lb	----	----
Permeability	Room Temp.	Helium Leak Tight	-----

*Extracted from Reference 4.

TABLE 2

EFFECT OF DEPOSITION TEMPERATURE ON THE
PHYSICAL PROPERTIES OF PYROLYTIC GRAPHITE
AT ROOM TEMPERATURE*

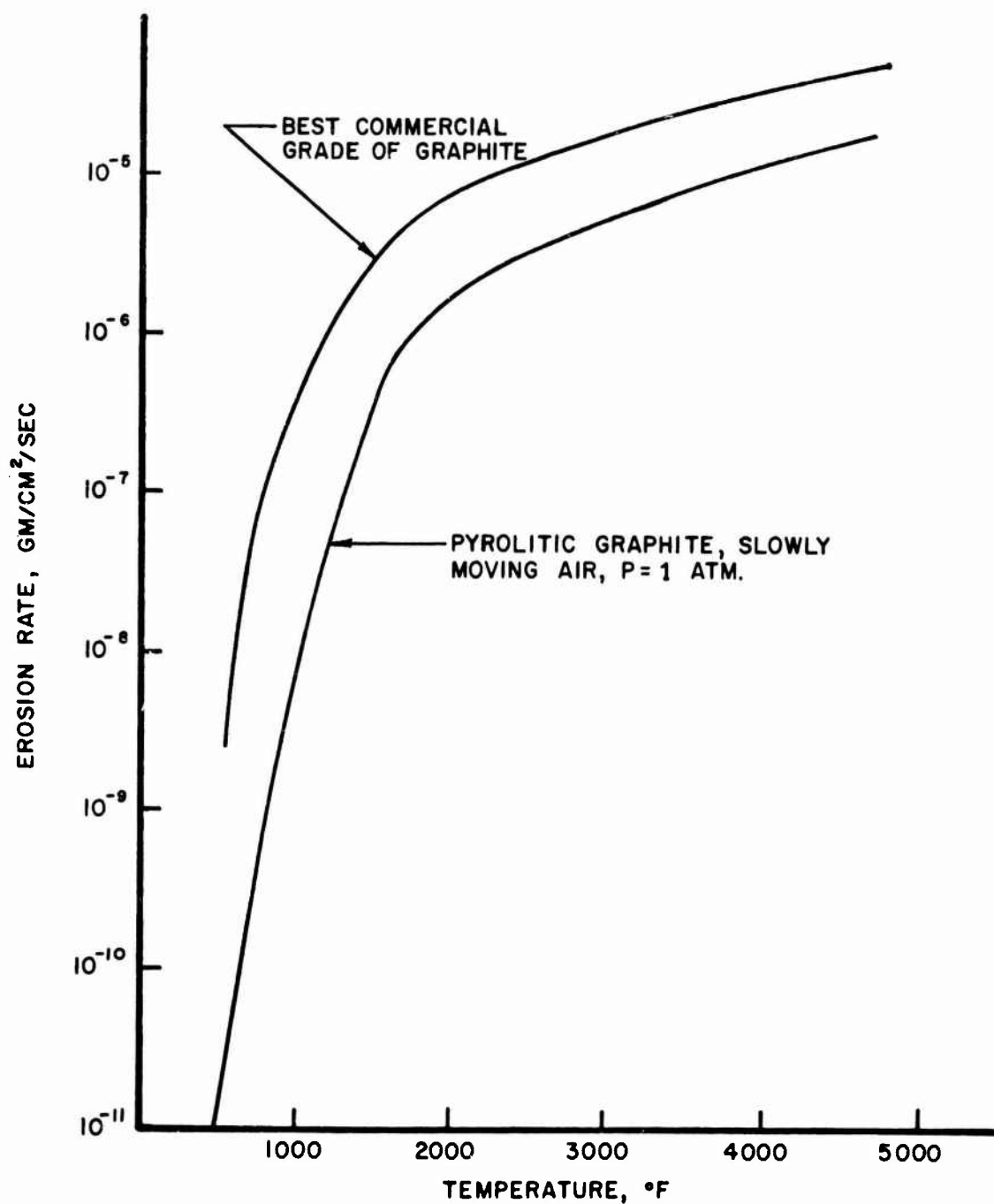| TEMPERATURE OF DEPOSITION ° R	THERMAL CONDUCTIVITY "a" DIRECTION BTU-FT/FT²/HR/° F	ELECTRICAL RESISTIVITY OHM-FT		THERMAL EXPANSION COEFFICIENT, 68-1742° F "a" DIRECTION FT/FT/° F
		"a"	"c"	
2440	---	1.3×10^{-4}	8.9×10^{-3}	1.3×10^{-6}
2620	---	-------	--------	1.2×10^{-6}
2800	14.5	7.2×10^{-5}	1.4×10^{-2}	1.5×10^{-6}
2980	51.4	5.3×10^{-5}	1.4×10^{-2}	1.4×10^{-6}
3160	265.8	1.2×10^{-5}	1.4×10^{-2}	0.6×10^{-6}
3340	323.6	7.8×10^{-6}	1.4×10^{-2}	0.6×10^{-6}
4060	---	6.6×10^{-6}	1.6×10^{-2}	0.6×10^{-6}

*Extracted from Reference 5

6

Figure 3. Comparison of Oxidation-Erosion Rate Data for Graphite

SECTION III

EXPERIMENTAL EQUIPMENT AND FACILITY

1. TEST MATERIAL

The material used was thin pyrolytic graphite foil purchased from High Temperature Materials, Inc. This foil is flexible, highly anisotropic (being deposited at temperatures of 4450°R), and is easily worked. In order to determine the mass loss over a period of time, a strip of graphite was weighed before and after it was electrically heated in a controlled atmosphere.

Strips of graphite 0.010 inch thick were cut approximately 1/4 inch wide and 4 inches long. The same material, but not the same strip, was used for all the testing. The material was checked for loss in weight due to outgassing in a vacuum with no electrical power added and it was determined that there was no weight change.

The strips were placed between two electrodes and heated electrically to the desired temperature in the preset ambient pressure. The method of connection is shown in Figure 4. The electrodes were water-cooled stainless steel. This approach worked satisfactorily with virtually no contact resistance at the connections.

2. VACUUM CHAMBER

The vacuum chamber was a three-inch-diameter Pyrex tube. The end flanges were of polished aluminum with Teflon seals between the flanges and the Pyrex. The outgassing of these materials is low and there is very little water adsorption on the surfaces. This is desirable because if other gases were pulled off the test surfaces under vacuum conditions, it could lead to erroneous and unpredictable interactions with the graphite. The feed-throughs and gas lines were well sealed. A blank-off vacuum of 10^{-5} Torr was achieved. The overall schematic is shown in Figure 5 with a photograph of the actual apparatus shown in Figure 6. A mechanical pump was used for rough evacuation, down to 10^{-2} Torr, and a two-inch diffusion pump was used for the final evacuation.

3. POWER SUPPLY AND INSTRUMENTATION

The power used was supplied by a Miller Vickers Controlarc d.c. power supply, a photograph of which is shown in Figure 7. Each unit has a maximum power output of 16 kw at 40 volts and 400 amps. They have continuous variation of power control so that it was possible to achieve any desired temperature on the test specimen. The instrumentation used included the following: optical pyrometer, voltmeter, ammeter, pressure gauges, laboratory balance, thermocouple, and pressure regulator.

The measurement of temperature at high levels is perhaps one of the most difficult assignments in which to achieve a high degree of accuracy. Because of the temperatures involved in the experiment and the material, the only practical way to determine the temperature was with an optical pyrometer. The radiation shielding served not only to keep the Pyrex temperature down but also aided in the pyrometry. The temperature could essentially be considered the same as a blackbody temperature because of the high emissivity of graphite at these temperatures and the small hole in the shields. The pyrometer used was a "Pyro" Micro Optical Pyrometer which is designed primarily for use in laboratory applications where accuracy is a prime consideration.

Since temperature was one of the most crucial parameters, all efforts were taken to achieve the greatest possible accuracy. The pyrometer itself was calibrated immediately prior to use on this test. The instrument reading could be repeated to an accuracy of within 15° F. The effect of the Pyrex and radiation shielding was calibrated in the following manner. The temperature of a clear glass tungsten filament light bulb was taken with no obstructions. The Pyrex tube and shielding was then put around the bulb in an identical condition, and the two temperatures were compared. A plot of temperature of reading was made versus the actual temperature.

This correction was then applied to the data points. The maximum correction was small, approximately 80° F. The total possible error is estimated to be less than 40° F.

The voltage was read off a Weston Voltmeter with an accuracy of reading of 0.1 volts. The current was taken from an ammeter with an accuracy of reading of 0.1 amperes. These instruments were calibrated immediately prior to conducting the tests.

The weights were taken on a laboratory precision balance with an accuracy of 0.0001 grams.

The gas pressure was taken on three different instruments. The ultralow pressure range was covered by a Phillips Gauge, the range of 0.1-760 Torr was covered with a Wallace and Tiernan pressure gauge, and for pressures greater than one atmosphere a 0 to 1600 Torr gauge was used. The overlap in the ranges of the different gauges contributes to the credibility of the measurements since the readings were identical in the overlap region.

A chromel-alumel thermocouple was used on the Pyrex tube. This had no direct effect on the results but merely served as a monitor of the glass temperature to preclude exceeding the design safety limits.

4. TEST GAS

The gases used were standard laboratory commercial grade helium and hydrogen. Pressure regulators were put on the bottles with a small needle valve on the downstream side of the regulator. The bottles were connected to the experimental rig with Polyflo tubing. The gas was analysed for impurities; the results are given and discussed in Section VI. A photograph of the complete apparatus is shown in Figure 8.
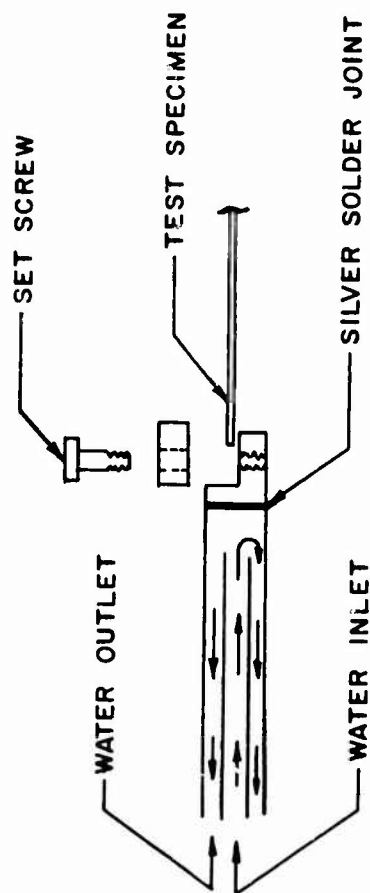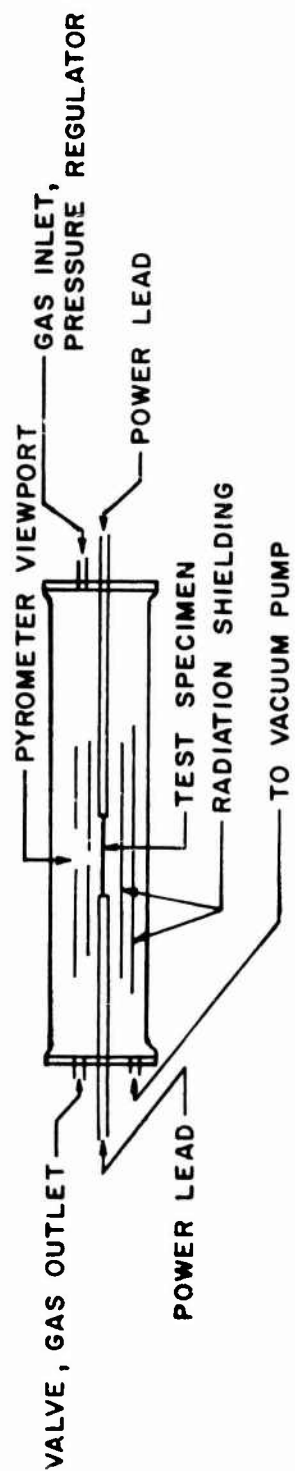
Figure 4. Schematic of Electrode Attachment Method

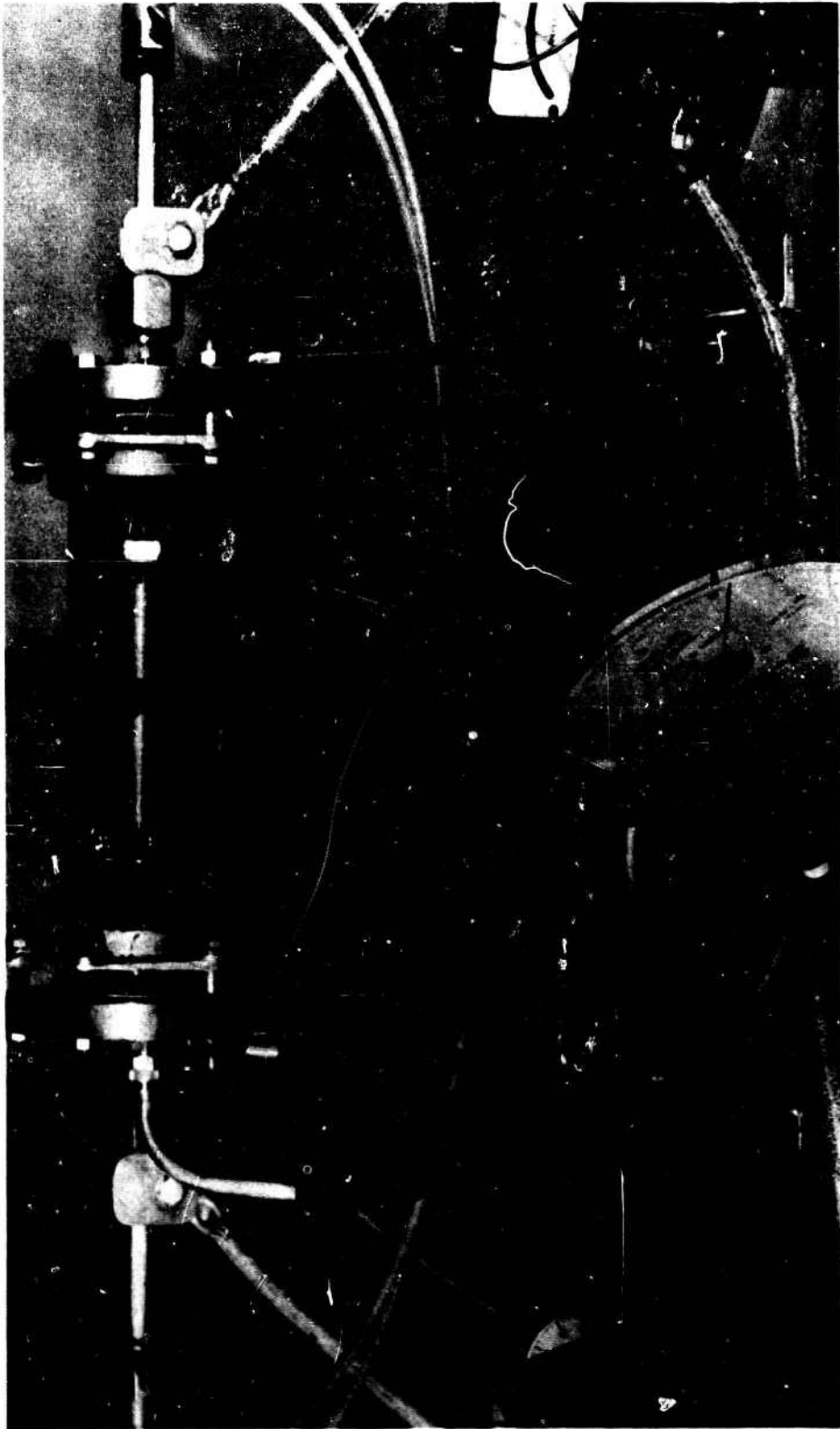Figure 5. Schematic of Test Apparatus
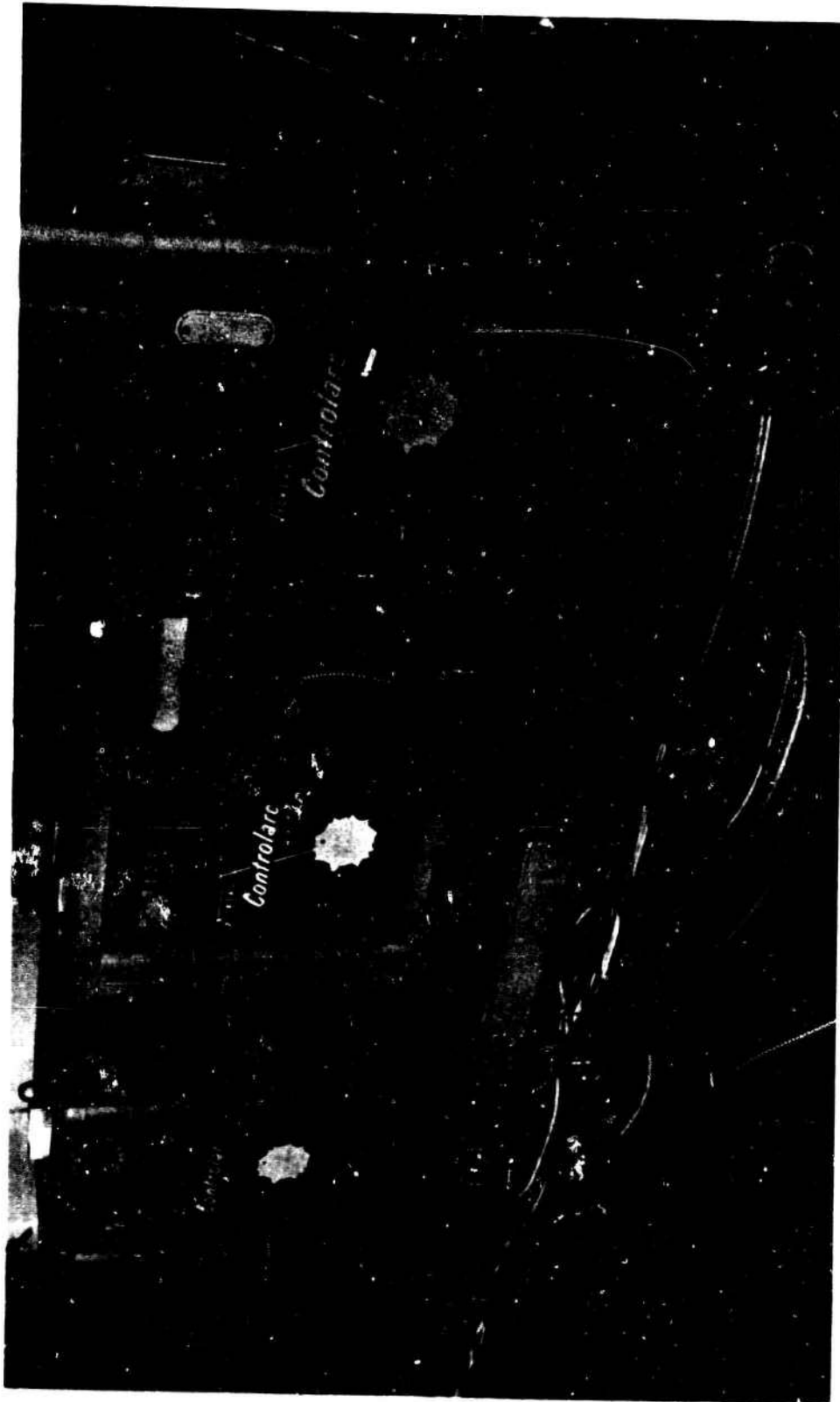
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Figure 6. Close-Up of Vacuum Chamber

11

Figure 7. D. C. Power Supplies Used on Test

SECTION IV

EXPERIMENTAL PROCEDURES

The procedures followed in the helium and hydrogen tests were nearly identical. To aid future investigators and to provide a basis for critical evaluation of this study, a deta'' 'escription of a typical helium test will be g 'n.

1. HELIUM TESTING

A pyrolytic graphite strip was carefully weighed on the laboratory balance and then placed between the two electrodes in the chamber. The chamber was evacuated and then refilled with helium. The chamber was then evacuated again to a very low pressure. This procedure was repeated three times so that any percentage of residual air would be negligible when compared with the helium present. The desired pressure of helium was then allowed into the chamber.

Voltage was then applied to the strip and the temperature monitored. The specimen was brought to the desired temperature by adjusting the voltage and current. This was accomplished quite simply because of the sensitivity of adjustment in the power supply. The pressure which increased because of the heating it receives from the specimen was adjusted back to the desired value. After a period of time the heating current was shut off, the time noted, and the specimen carefully removed. It was then reweighed on the same balance and the difference used to calculate the rate of mass loss.

A very small flow was maintained in the chamber. The overall velocity was estimated to be less than 0.5 ft/min. The reasons for the small flow were to keep the tube from overheating and to remove the products of reaction from the inside of the chamber.

The temperature distribution on the sample was observed without the radiation shielding. The ends of the foil are cool, of course, since they are held by the water-cooled electrodes. The temperature gradient at the ends was very sharp, however, and the area at the lower temperature was very small when compared

to the overall length. The foil was 4 inches in length. By using the pyrometer to scan the length of the foil, we found that the foil achieved a steady-state temperature as close as 0.0625 inch from the electrode attachment. Therefore, the distance between the electrodes is approximately the heated length and can be measured accurately.

Time at temperature varied depending on the expected sublimation rate. It was imperative that enough material be removed by sublimation so that the error in the weight measurement be small compared to the amount of material removed. The configuration used was fortuitous in that it exposes the maximum surface area for a given weight. This has the effect of cutting down the time required to achieve an appreciable change. The longest run time was 7 hours, which was the amount of time needed to get a measurable weight difference at the lowest temperature using helium.

2. RESISTANCE CHANGE METHOD

One method which was used to get a periodic check of the mass loss during the test without stopping and disassembling the electrode attachments was to monitor the resistance of the foil. Keeping in mind that the temperature is kept constant at all times, we can write the resistance equation for the foil as

$$R' = \frac{\sigma L}{A} \tag{1}$$

Taking logarithms and differentiating we obtain

$$\frac{dR'}{R'} = \frac{d\sigma}{\sigma} + \frac{dL}{L} - \frac{dA}{A}$$

The mass of the strip is simply,

$$m = \rho AL \tag{2}$$

By similar methods,

$$\frac{dm}{m} = \frac{d\rho}{\rho} + \frac{dA}{A} + \frac{dL}{L}$$

But $d\sigma$, $d\rho$, and dL are equal to zero; using this and substituting

$$\frac{dR'}{R'} = \frac{-dm}{m} \qquad (3)$$

Therefore, for small changes in mass at constant temperature the effect will show up in the resistance of the element. It should be observed that this method assumes a uniform strip thickness. To be of maximum effectiveness the voltage and current measuring devices should be of the same degree of accuracy as the balance.

3. ACCURACY CONSIDERATIONS

The linearity of the method of determining weight change was checked with three different runs at identical temperatures and pressures. The only difference was the length of test time, these being 1 hour, 3 hours, and 7 hours. The mass loss rate was found to agree within 7% on these runs.

When removing the foil for weighing, the graphite tended to stick to the electrode, so the electrode had to be carefully scraped of all particles. These particles themselves formed less than 10% of the mass loss, and since care was taken, the error from this adhering is expected to be less than 1%.

The outgassing of impurities in the foil, was checked. In this material no loss in weight occurred due to outgassing under a vacuum at room temperature. Because of the nature of the material and the care taken in handling, impurities in or on the material which would outgas are expected to be negligible.

4. HYDROGEN TESTING

The testing of the rate of mass loss in hydrogen followed a very similar procedure to that for helium. Helium was used as the flushing gas, with three evacuations and refillings. On the third evacuation however, hydrogen was used to fill the chamber to the desired pressure. The same precautions were taken as with helium to insure accuracy. The only difference between the tests is that the hydrogen test times were considerably less because the reaction rate with hydrogen is much higher than that with helium.

If the foil broke during a test due to a structural defect, a hotspot, or a localized reaction, an arc would usually occur with catastrophic results to the electrode. For this reason, we limited the test time to no longer than necessary to achieve a measureable mass change.
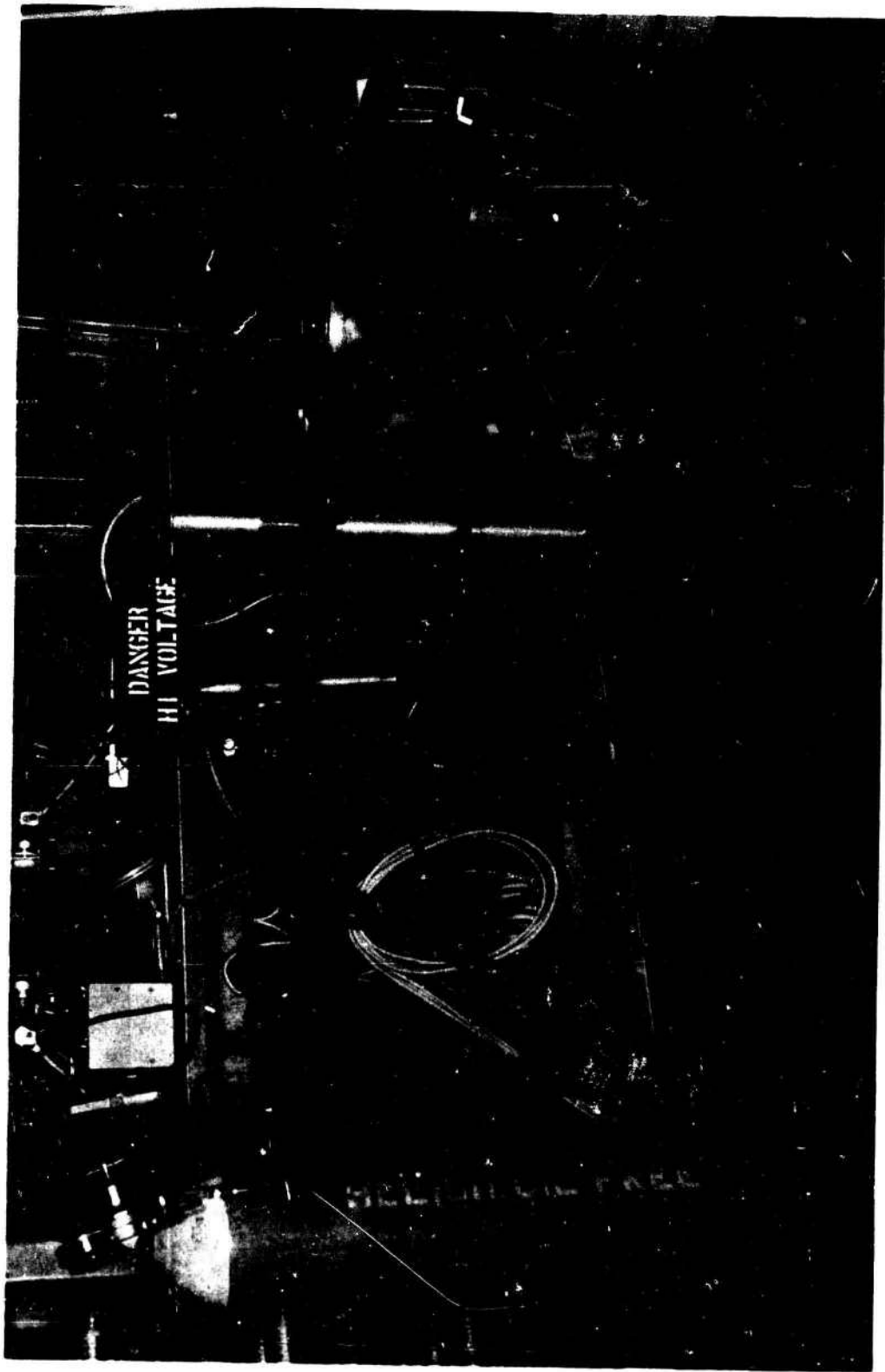
Figure 8. Overall Test Apparatus

15

SECTION V

RESULTS

1. HYDROGEN

The test results using hydrogen as the ambient gas indicate that the mass loss rate is orders of magnitude greater than those in the helium atmosphere. The measured mass loss rate as a function of temperature at three different pressures are presented in Figure 9. The time of test to get an appreciable mass change was on the order of one hour. The highest power consumption was on the order of one kilowatt at 4100°R.

It has been found that in the oxidation of graphite mass flow is not extremely critical if the flow rate is low. With this in mind, we postulated that the effect of flow on the hydrogen-graphite reaction would be similar. Two runs were made with identical conditions except for the flow velocity past the foil. The results were then compared. The two velocities, while not measured precisely were estimated at 0.5 ft/min and 2.0 ft/min. Agreement in reaction rate was within 5%.

2. HELIUM

The mass loss rates using helium as the ambient gas are presented in Figure 10. The rate is plotted versus temperature for four ambient pressures. The mass loss rate is closely tied to both temperature and pressure in the range investigated. The effect of helium pressure increase, in general, appears to suppress the loss rate. With hydrogen the reverse was true in that the mass loss rate increased sharply with an increase in pressure. If the rate changes had been of the same order of magnitude, it perhaps would be possible to select an optimum point. They differ by orders of magnitude, however, so this is not possible in this range.

3. THEORETICAL SUBLIMATION

The sublimation in a perfect vacuum can be theoretically calculated using the Langmuir equation which is derived from the kinetic theory of gases. This equation assumes that none of the emitted molecules returns to the parent source. This is the limiting case as the number of gas molecules above the subliming surface goes to zero. These molecules, by collision, with emitting molecules, would return some to the surface. The equation is

$$r = .0785 \; P_v a \sqrt{\frac{M}{T}} \qquad (4)$$

The sublimation rate is given in gm/cm^2-sec in the above equation when the vapor pressure is given in Torr, and the temperature in °R. The vapor pressure for carbon over a wide range is available in the literature (10). That which was not available was obtained by extrapolation, using the standard vapor pressure equation, which has found to provide a good empirical fit.

$$Log_{10} \; P_v = \frac{a}{T} + b \qquad (5)$$

The constants a and b were evaluated from given data near 4000°R for extrapolation of vapor pressure in the range 3000-4000°R. The vapor pressure for carbon as a function of temperature is given in Figure 11. The evaporation coefficient can be taken as approximately unity for carbon (11). With this information, the Langmuir equation can be used to determine mass loss rate of carbon as a function of temperature. This is presented in Figure 12 as the theoretical mass loss rate in a perfect vacuum.
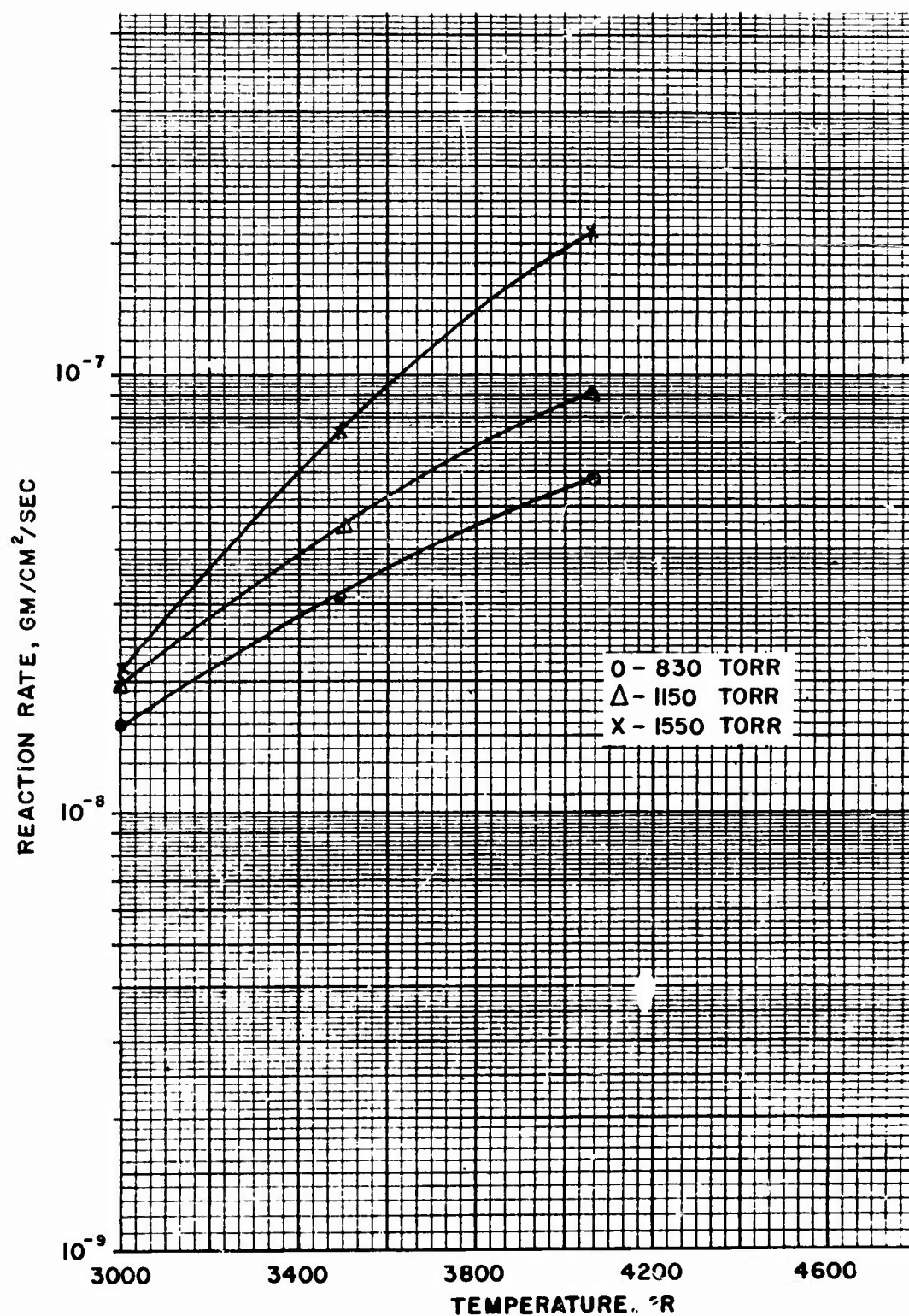
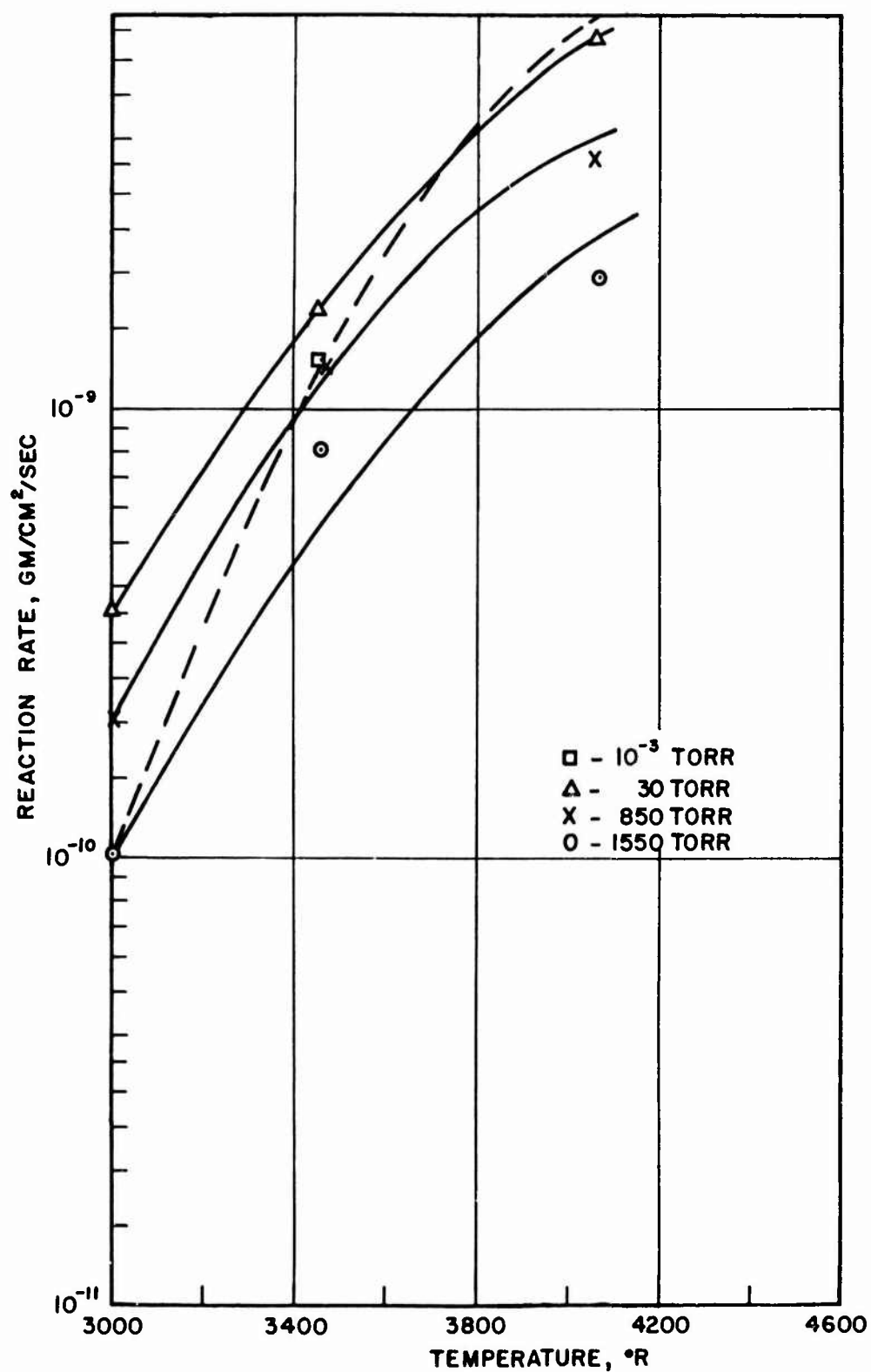Figure 9. Measured Reaction Rate in Hydrogen

17

Figure 10. Measured Reaction Rate in Helium

18

SECTION VI

DISCUSSION OF TEST RESULTS

1. HYDROGEN

The purpose of the helium testing was to provide a base on which to judge the reactivity of hydrogen. The difference between the mass loss in hydrogen and the mass loss in helium at identical temperature and pressure conditions would be directly attributable to the hydrogen-carbon reaction. This objective served another purpose, it developed, because of the relatively high degree of impurity that exists in the commercial grade of gases available in the laboratory. The air impurity in hydrogen is approximately the same as it is in helium. Impurity from water vapor and other gases was negligible, but the oxygen impurity affected the results of the helium tests most.

The results with hydrogen are considered to be quite accurate. Since the impurity level is approximately the same in hydrogen as it is in helium and since the reaction rate with hydrogen is orders of magnitude greater than with helium, the error due to impurities in the hydrogen should be less than 1%. The other considerations in accuracy have already been discussed.

The rate of mass loss goes up rather steeply with increasing hydrogen pressure. The mass loss rate also increases as the foil temperature is increased. The maximum temperature for any run was 4100°R because of the heat limitation of the Pyrex and also because hotspots frequently developed above these temperatures burning through the foil, striking an arc, and melting the end of the electrode. A heavier foil, different configuration, and cooled vacuum chamber should be used for work at temperatures above these. It is suspected that above these temperatures the mass loss rate would continue to rise but that the rate of increase would lessen, following the trend of the vapor pressure curve. The trends with both temperature and pressure is not at all unexpected. As pressure increases, more hydrogen is available at the hot graphite surface, increasing the mass loss rate. As temperature of the foil increases, more carbon atoms are emitted to react in the boundary layer with hydrogen molecules.

The effect of flow, while not critical at low flow rates, would become significant as turbulence is reached. If diffusion of reactant products out of the boundary layer is considered to be the prime mass transfer mechanism, then those parameters which affect the diffusion rates would be limiting factors. All flow conditions which determine the boundary layer would then influence the mass loss rate of the graphite to the extent that they influence the boundary layer form and thickness. This theory is considered in more detail in the discussion of the helium results. The results with hydrogen are useful because they provide mass loss data over temperature and pressure ranges frequently encountered.

2. HELIUM

The results with helium follow the same temperature trend as with hydrogen, but the pressure effect is quite different. An increase in pressure, in general, tends to decrease the loss rate except at very low vacuum. This result is reasonable because at higher pressures more helium molecules are available for collision with emitted carbon molecules; hence, more carbon molecules are returned to the surface, thereby decreasing the net mass loss.

The accuracy of the points at 10^{-10} gm/cm^2 -sec is not precise. A test time of one full day at this low temperature did not produce a change of more than 0.0001 grams, which was the accuracy of the balance. Therefore these points should be accepted as upper limits rather than precise values in themselves.

If a comparison is made between the theoretical maximum in a perfect vacuum and values obtained experimentally under inert pressure, a surprising result is found. In almost all cases the theoretical maximum

is less than the measured values, indicating that if the mechanism is pure sublimation the experimental results are high. The explanation is quite probably in the impurity content of the test gas.

The oxygen impurity, 0.003 moles, introduces a substantial partial pressure of oxygen at the pressures being tested. At the 830 Torr pressure level, this corresponds to a partial pressure of 2.5 Torr or 3.2×10^{-3} Atm. Comparing this to the results of Strickland-Constable (12), who did research on the oxidation of graphite at low oxygen pressure, we find that at 4000°R and 2.5 Torr he indicates a rate of mass loss of approximately 7.5×10^{-7}. This rate is considerably higher than the rate of 3.8×10^{-9} gm/cm^2/sec measured by the author at identical temperature and oxygen pressure.

The discrepancy can be explained in the following theory. It is probable that the dominant factor in oxidation or reaction is the diffusion of reactant products from the boundary layer volume surrounding the test specimen. It is also quite probable that the principal mechanism of mass loss in these helium tests was the reaction of low partial pressure oxygen with graphite. The latter statement has two justifications. The first is that a large amount of data is available showing appreciable graphite reaction with low pressure oxygen. The other is based on the observation that the chamber was immaculately clean after the high pressure helium runs, but after comparable mass loss in the very low vacuum run, a deposit of soot was noticed throughout the chamber. This would indicate that perhaps carbon dioxide was the product in the pressure runs while carbon atoms themselves were the loss under vacuum.

In examining the diffusion laws to try to correlate these results, we must start with the general transient, one-dimensional mass transfer equation:

$$\partial C_A / \partial \theta = D_v \, \partial^2 C_A / \partial y^2 \qquad (6)$$

Steady state can be assumed since the concentration at a point is not a function of time. A total differential equation is then produced which can be integrated to yield.

$$r_A = -D_v \, dC_A / dy \qquad (7)$$

Consider the case where carbon dioxide, denoted as the A species, diffuses through a stationary gas, denoted as the B species. In this experiment the stationary gas would be high pressure helium and in the case of the Strickland-Constable experiment it would be low pressure oxygen. The reactant product is assumed to be diffusing from the test foil material through the boundary layer to the main bulk flow where the product concentration is kept at zero. Since carbon dioxide is diffusing from the boundary layer, there must be a partial pressure gradient out of the boundary layer. (Carbon monoxide is also a product, but for the purposes of this comparison we will assume the product to be entirely carbon dioxide.)

The species concentration can be related to the partial pressure by the ideal gas law,

$$P_A = C_A \, RT \qquad (8)$$

Taking the derivative and substituting in the diffusion equation yields,

$$r_A = \frac{-D_v}{RT} \frac{dP_A}{dy} \qquad (9)$$

The total pressure of the system is considered to be constant,

$$P = P_A + P_B = \text{Constant}$$

Since there is diffusion of carbon dioxide out of the boundary layer, there must be a counter flow of helium into the boundary layer given by,

$$r_B = \frac{-D_v}{RT} \frac{dP_B}{dy}$$

20

but,

$$- \frac{dP_A}{dy} = \frac{dP_B}{dy}$$

hence by substitution,

$$r_B = \frac{D_v}{RT} \frac{dP_A}{dy} \tag{10}$$

If we consider that the amount of helium at the boundary layer interface is invariant, then there must be a bulk flow of both helium and carbon dioxide outward to replenish the supply at the interface. The presence of a percentage of carbon dioxide in the bulk flow will effectively increase the rate of mass transfer of carbon dioxide. This flow of carbon dioxide can be given by

$$r_A' = \frac{C_A}{C_B}(-r_B) = \frac{P_A}{P-P_A}(-r_B) =$$

$$\frac{P_A}{P-P_A}\left(-\frac{D_v}{RT} \frac{dP_A}{dy}\right)$$

The total flux of carbon dioxide out of the boundary layer is then given by the sum of the diffusion because of the partial pressure gradient and the bulk flow component

$$r_{At} = r_A + r_A' = -\frac{D_v}{RT}\left(1 + \frac{P_A}{P-P_A}\right)\frac{dP_A}{dy} \tag{11}$$

Integrating from the reacting surface to the boundary layer edge gives

$$r_{At} = \frac{D_v}{RT} \frac{P}{y_2 - y_1} Ln \cdot \frac{P-P_{A2}}{P-P_{A1}} \tag{12}$$

This equation is the governing equation for one-directional single-species diffusion through a stationary gas.

The following assumptions were made in an effort to correlate the results of these experiments with results of tests conducted by previous investigators at identical temperatures and oxygen pressures.

a. This experiment differed mainly in that a large amount of helium was present in the ambient gas.

b. The controlling mass transfer mechanism is oxidation and product diffusion through the boundary layer.

c. The diffusion coefficients vary approximately directly as the 3/2 power of temperature and inversely as the total pressure.

d. The partial pressure of carbon dioxide outside of the boundary layer is zero.

e. The ratio of the boundary layer thickness in the two experiments is of order unity.

f. The concentration of carbon dioxide is of the same order in both experiments and small in comparison to the total pressure.

g. The distribution of temperature across the boundary layer is approximately equal in both cases.

Since what is desired is an order of magnitude approximation, these assumptions are justified. With these assumptions, the theoretical mass flux ratio between this experiment and that of Strickland-Constable becomes

$$\frac{r_{A1}}{r_{A2}} = \frac{D_{o1}}{D_{o2}} \frac{P_2}{P_1} \tag{13}$$

The diffusivity of carbon dioxide into oxygen is approximately 0.64 ft^2/hr while the diffusivity of carbon dioxide into helium is 1.76 ft^2/hr at standard temperature and pressure (13). Substituting these values along with the total pressures of both experiments, the theoretical ratio should be 8.8 x 10^{-3}. The actual ratio between the two results is approximately 5.1 x 10^{-3}. They are therefore of the same order of magnitude and comparable. This experiment, in the opinion of the author, lends support to the diffusion limited theory of reaction.
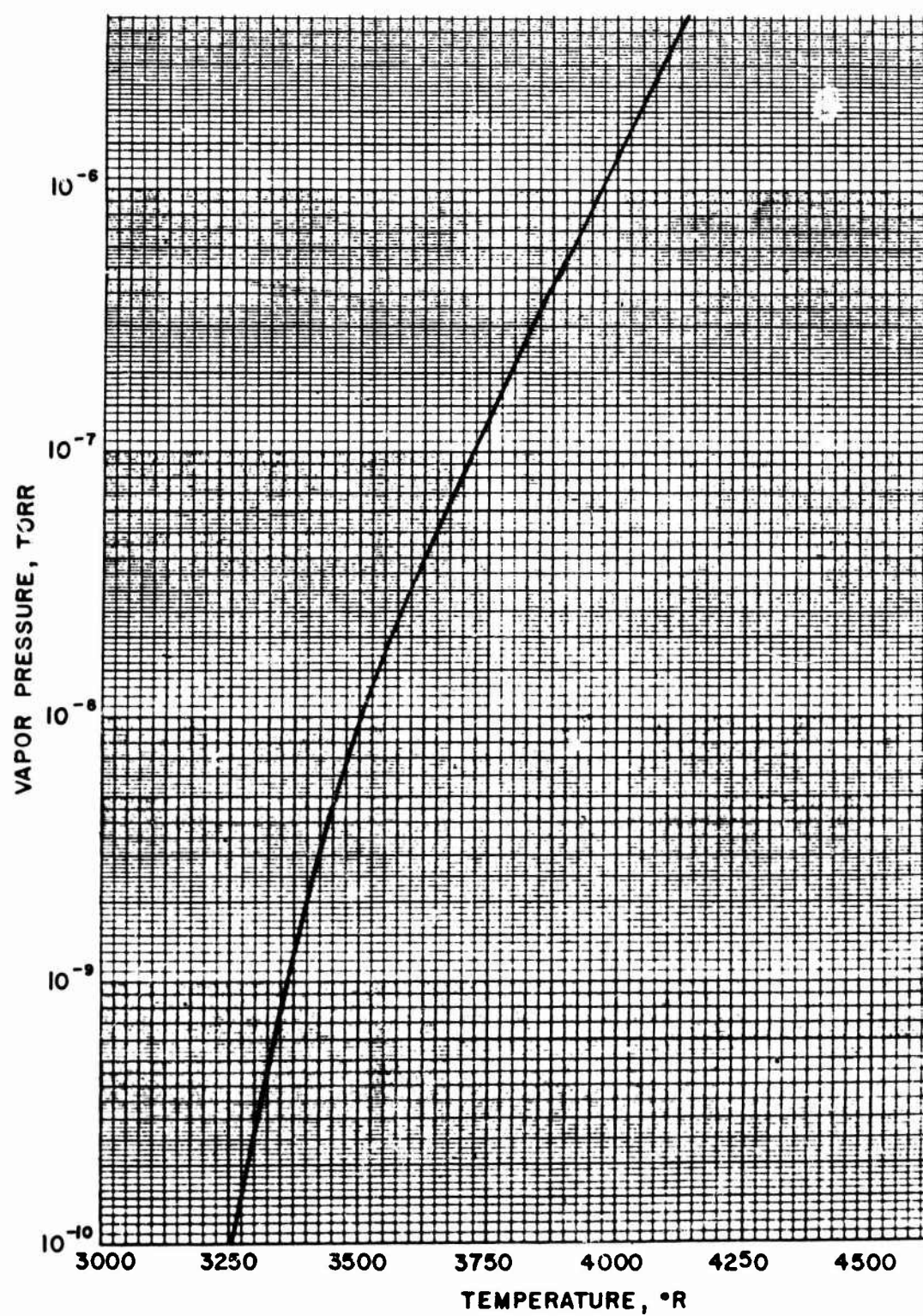
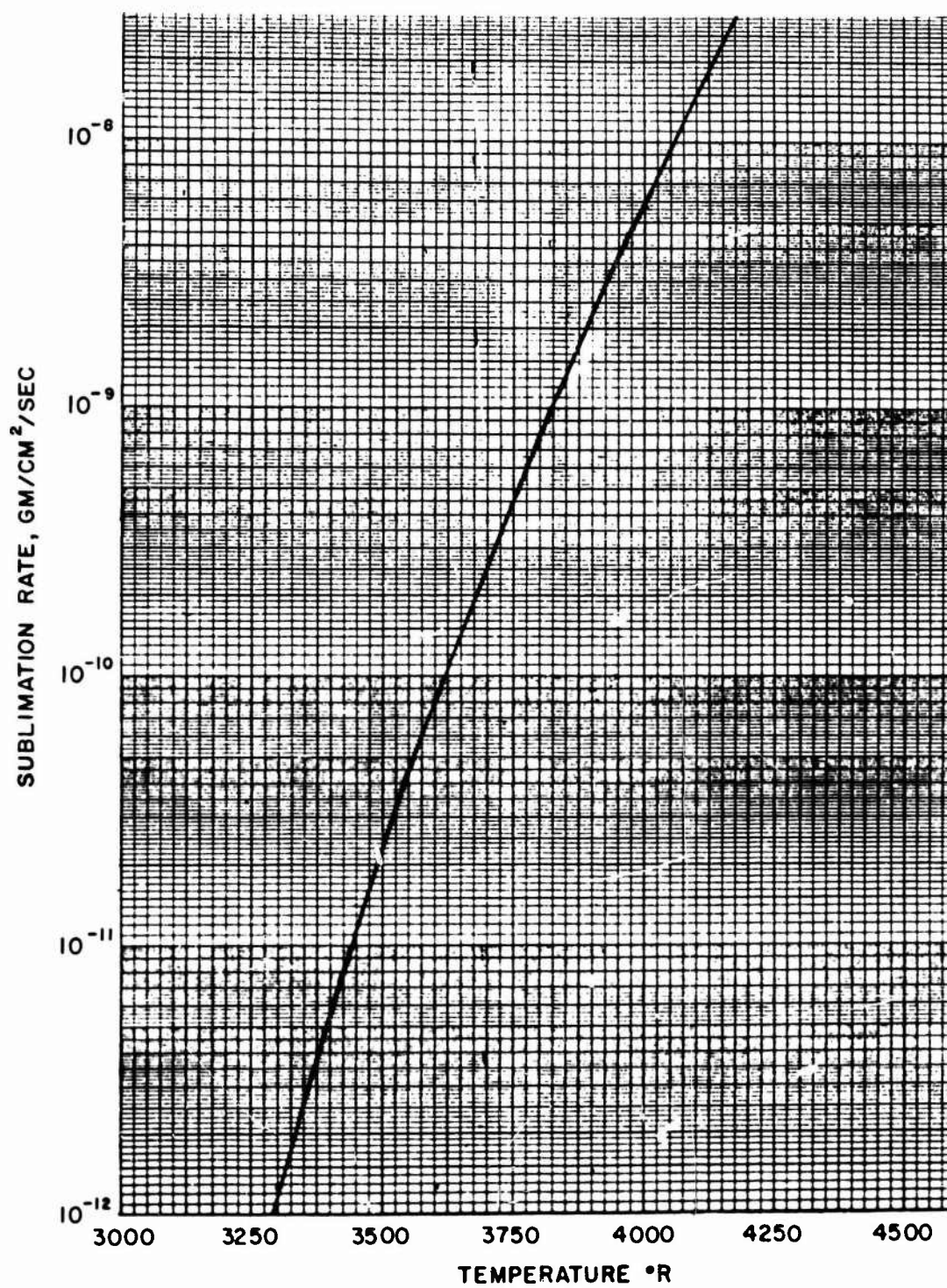Figure 11. The Influence of Temperature on Vapor Pressure of Graphite (Equation 5)

Figure 12. Theoretical Sublimation of Carbon in a Perfect Vacuum, (Equation 4)

SECTION VII

CONCLUSIONS

The results of this experiment show that the hydrogen-carbon reaction rate on pyrolytic graphite is not prohibitive. A typical measured value of about 10^{-7} gm/cm^2-sec at 4000°R and 1 atmosphere pressure is small when considered for use in most designs. It does, however, limit life for a foil such as that used in this testing. An increase of temperature or pressure will increase the hydrogen-carbon reaction rate.

The helium results are dominated by the oxygen impurity in the gas used. An increase of total pressure in the helium environment, in general, suppresses the mass loss rate from the graphite foil. A comparison of low partial pressure oxidation with results of previous experiments lends support to the diffusion limited theory of reaction.

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This report presents the results of an investigation into the mass loss rate from a pyrolytic graphite foil at various temperatures and pressures. The mass loss in a hydrogen atmosphere is presented at temperatures from 3000 to 4100°R and pressures from 830 to 1550 Torr. The mass loss rate in an inert helium atmosphere at the same temperatures and at pressures from 10^{-3} to 1550 Torr is presented. The experimental data is compared to the theoretical rate and, when applicable, to the work of previous experimenters.

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